

APPLICATION

of

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for

UNITED STATES LETTERS PATENT

on

**IMPROVED COPPER BATH FOR ELECTROPLATING FINE
CIRCUITRY ON SEMICONDUCTOR CHIPS**

Docket No. 03RSC004

Assigned to:

Innovative Technology Licensing, LLC

BACKGROUND OF THE INVENTION

Field of the Invention

This invention is concerned with fabrication of copper integrated circuits on semiconductor chips, and in particular with electrodeposition of copper circuitry.

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Description of the Related Art

The electronics industry is transitioning from aluminum to copper as the basic metallization for semiconductor integrated circuits (IC's) in order to increase device switching speed and enhance electromigration resistance. The leading technology for fabricating copper circuitry on semiconductor chips is the "Damascene" process (P. C. Andricacos, Electrochem. Soc. Interface, Spring 1999, p.32; U. S. Patent 4,789,648 to Chow et al.; U. S. Patent 5,209,817 to Ahmad et al.). In this process, vias are etched in the chip's dielectric material, which is typically silicon dioxide, although materials with lower dielectric constants are under development. A barrier layer, e.g., titanium nitride (TiN), tantalum nitride (TaN) or tungsten nitride (WN_x), is deposited on the sidewalls and bottoms of the trenches and vias, typically by reactive sputtering, to prevent Cu migration into the dielectric material, which would degrade the device performance. Over the barrier layer, a thin copper seed layer is deposited, typically by sputtering, to provide enhanced conductivity and good adhesion. Copper is then electrodeposited (electroplated) into the trenches and vias. Copper deposited on the outer surface, i.e., outside of the trenches and vias, is removed by chemical mechanical planarization (CMP). A capping or cladding layer (e.g., TiN, TaN or WN_x) is applied to the exposed copper circuitry to suppress oxidation and migration of the copper. Alternative barrier/capping layers based on electrolessly deposited cobalt and nickel are under investigation [e.g., A. Kohn, M. Eizenberg, Y. Shacham-Diamand and Y. Sverdlov, Mater. Sci. Eng. A302, 18 (2001)]. The "Dual Damascene" process involves deposition in both trenches and vias at the same time. In this document, the term "Damascene" also encompasses the "Dual Damascene" process.

Damascene copper electrodeposition is typically performed from an acid copper sulfate electroplating bath, which requires a minimum of two types of organic additives to provide good deposit properties and complete filling of the trenches and vias. The

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"suppressor" additive (also called the "polymer", "carrier", or "wetter", depending on the bath supplier) is typically a polymeric organic species, e.g., high-molecular-weight polyethylene or polypropylene glycol, which adsorbs strongly on the copper cathode surface, in the presence of chloride ion, to form a film that sharply increases the overpotential for copper electrodeposition [M. R. H. Hill and G. T. Rogers, *J. Electroanal. Chem.* 86, 179 (1978)], i.e., suppresses the rate of copper deposition at a given potential. This greatly enhances the throwing power and leveling characteristics of the bath, and inhibits uncontrolled copper plating that would result in powdery or nodular deposits. The "anti-suppressor" additive (also called the "brightener", "accelerator" or simply the "additive", depending on the bath supplier) also adsorbs strongly on the copper surface and counters the suppressive effect of the suppressor so as to enhance the copper electrodeposition rate [W. O. Fritag, C. Ogden, D. Tench and J. White, *Plating Surf. Fin.* 70(10), 55 (1983)]. The anti-suppressor acts primarily as a catalyst and is not consumed rapidly in the electrodeposition process. As curvature develops in the copper deposit at the bottom edges of the Damascene features, the surface area is decreased, which increases the concentration of adsorbed anti-suppressor and accelerates deposition at the feature bottoms to produce "superconformal" deposition or "bottom-up" filling [D. Josell, D. Wheeler and T. P. Moffat, *Electrochem. & Solid-State Letters* 5(4), C49 (2002)].

For proper functioning of the acid copper sulfate additive system, a delicate balance between the suppressor and anti-suppressor additives must be maintained. In addition, it is necessary to control the concentration of chloride ion, which is known to be essential to the functioning of the suppressor and anti-suppressor additives in acid copper sulfate baths [e.g., J. D. Reid and A. P. David, *Plating Surf. Fin.* 74(1), 66 (1987); J. J. Kelly, C. Tian and A. C. West, *J. Electrochem. Soc.* 146(7), 2540 (1999)]. An imbalance in the additive system typically results in unacceptable voids or defect lines in the Damascene copper deposit, formed as the copper deposits on opposing sidewalls of the feature grow together (in the absence of bottom-up filling).

As the feature size for the Damascene process has shrunk below 0.2 μm , it has become necessary to utilize a third organic additive in acid copper sulfate baths in order to suppress overplating of the trenches and vias. Note that excess copper on Damascene plated wafers (called the "overburden") is typically removed by chemical mechanical planarization

(CMP) but the copper layer must be relatively uniform for efficient CMP removal. The third additive is called the "leveler" (or "booster", depending on the bath supplier) and is typically an organic compound containing nitrogen or oxygen that also tends to decrease the copper plating rate. The leveler is generally present at a relatively low concentration so that it is most effective at the outer surface of the wafer where it is effectively replenished by solution agitation.

The concentrations of organic additives in copper electroplating baths are typically determined from the effect that they exert on the copper electrodeposition rate measured via cyclic voltammetric stripping (CVS) analysis [D. Tench and C. Ogden, J. Electrochem. Soc. 125, 194 (1978)]. In the CVS method, the potential of a platinum rotating disk electrode is cycled in the plating bath between fixed potential limits so that metal is alternately plated on and stripped from the electrode surface. The copper electrodeposition rate is generally determined from the voltammetric stripping peak area for the rotating electrode (A_r), which corresponds to the charge required to anodically strip the copper deposited during a given cycle. To improve measurement precision, A_r is typically normalized via division by the stripping peak area for the stationary electrode in the same solution (A_s), or via division by $A_r(0)$ measured for a background electrolyte without organic additives. The CVS method was first applied to control copper pyrophosphate baths (U. S. Patent 4,132,605 to Tench and Ogden) but has since been adapted for control of the various additive components in acid copper sulfate baths. For example, the acid copper suppressor concentration can be determined by CVS response curve or dilution titration analysis [W. O. Freitag, C. Ogden, D. Tench and J. White, Plating Surf. Fin. 70(10), 55 (1983)], and the anti-suppressor concentration can be determined by the linear approximation technique (LAT) or modified linear approximation technique (MLAT) described by R. Gluzman [Proc. 70th Am. Electroplaters Soc. Tech. Conf., Sur/Fin, Indianapolis, IN (June 1983)].

A major disadvantage of the acid copper sulfate system for Damascene plating is the complicated additive system, whose components must be closely controlled to obtain acceptable deposits. Close control is difficult to attain since the various additive species are generally present at very low concentrations and exert synergistic effects. Plating bath suppliers typically provide organic additives in the form of solutions that may contain additives of more than one type (as well as inorganic species), which exacerbates the

difficulty of controlling the additive system. In addition, additive components may be comprised of more than one chemical species, and the suppressor additive generally involves a range of molecular weights.

Furthermore, additive breakdown products tend to accumulate in the plating bath and interfere with functioning of the additive system. Such breakdown products, which include lower-molecular-weight suppressor species, must be monitored and periodically removed. Additive breakdown products are typically removed by bleeding off part of the plating bath and replacing it with fresh plating solution (bleed-and-feed), which is costly and environmentally undesirable.

Another disadvantage of the acid copper sulfate system for Damascene plating is that key properties of the deposit (grain size, hardness and electrical conductivity) undergo slow changes at ambient temperatures. To provide stable properties and maximum electrical conductivity within a short time, deposits are annealed (typically at about 200°C), which adds an extra processing step and increases costs.

Still another disadvantage of the acid copper sulfate system for Damascene plating is that the copper deposit tends to be relatively soft (large-grained). During CMP processing, soft copper tends to be removed faster than the surrounding dielectric material and, especially for wide trenches and bond pads, may “dish” and lose the planarity needed to facilitate bonding and minimize circuit electrical resistance. Soft copper also tends to exacerbate CMP erosion of copper and dielectric material in clusters of closely-spaced narrow trenches.

Still another disadvantage of the acid copper sulfate system for Damascene plating is that the deposit mechanical properties are strongly dependent on the substrate [R. Haak, C. Ogden, and D. Tench, *Plating Surf. Fin.* 68(10), p. 59 (1981); K. Abe, Y. Harada, and H. Onoda, *IEEE 98CH36173 Ann. Int. Rel. Phys. Symp.*, p. 342 (1998)]. Consequently, inconsistencies or changes in the barrier and seed layers may significantly affect the properties of the Damascene copper.

Still another disadvantage of the acid copper sulfate system for Damascene plating is that the plating bath is strongly acidic (typically, 10% sulfuric acid by volume). The strong acid tends to attack the copper seed layer, which is a particular problem for very narrow and/or deep Damascene features since the seed layer in this case is necessarily thin and may not be uniform. To avoid unacceptable thinning of the copper seed layer via acid attack, it is

often necessary to introduce the semiconductor wafer into the plating bath with electrical power applied, i.e., “hot”, which constrains the plating cell design and may not be totally effective.

One possibility for avoiding the complicated additive systems employed in acid copper sulfate baths is to utilize a copper plating bath based on an anion (pyrophosphate and cyanide, for example) that forms strong complexes with copper ions. In this case, the strongly complexing anion performs the function of suppressing the copper electrodeposition rate (raising the copper deposition overpotential) so that the polymeric suppressor additive employed in acid copper sulfate baths is not needed. A copper plating bath based on a strongly complexing anion (or anions) is termed a “complexed bath” or “complexed copper bath” herein. Complexed copper baths generally provide high throwing power (uniform deposit thickness over irregular-shaped substrates) and deposits with good mechanical properties, even without organic additives. Organic brightening and leveling additives are typically used in such baths to provide finer-grained deposits with enhanced brightness (luster) and improved mechanical properties, and to improve the uniformity and smoothness of deposits on irregular or rough substrates. The copper pyrophosphate bath has been widely used for electrodepositing uniform copper layers within through-holes (and blind vias) in printed wiring boards (PWB’s).

Brightening and leveling additives in the complexed copper baths of the prior art literature generally function by adsorbing on the copper surface and blocking growth sites so that the copper electrodeposition rate at a given electrode potential is suppressed further (beyond the suppression provided by strongly complexing anions). Within recessed areas of the deposit, the adsorbed additive species, which is typically present at low concentration in the bulk solution, becomes depleted as it is consumed in the copper electrodeposition process so that the rate of copper electrodeposition within the recessed areas increases. The additive species is less depleted on flat or protruded areas of the deposit, where it is more effectively replenished by solution flow produced by bath agitation, so that the copper electrodeposition rate remains substantially suppressed in these areas. More rapid copper deposition within deposit recesses tends to level and brighten the deposit. The increased overpotential provided by leveling/brightening additives also improves the bath throwing power (ability to provide uniform deposit thickness over irregular-shaped substrates).

Complexed copper baths employing the brightening/leveling additives of the prior art, which function by the suppression-depletion mechanism described above, have very limited utility for Damascene plating. Bottom-up filling by this mechanism requires that copper deposition be accelerated at the feature bottom by additive depletion during copper electrodeposition, and be suppressed on the feature sidewalls by additive replenishment via solution flow. Bath agitation produces negligible solution flow within the very narrow Damascene features of principal interest to the electronics industry (0.2 μm or less). Under the substantially stagnant conditions existing within narrow features, the additive is uniformly depleted over the surface during copper deposition and a conformal deposit is obtained. In this case, opposing feature sidewalls grow together, producing a void or defect line. The additive concentration gradient needed for bottom-up filling by the suppression-depletion mechanism can only be attained within relatively wide Damascene features, within which bath agitation produces substantial solution flow. In addition, for prior art additives used in strongly complexed baths, the feature aspect ratio (depth to width ratio) cannot be so large that substantial additive depletion occurs on the lower sidewall areas, causing opposing sidewalls to grow together to create a void or defect line.

A copper pyrophosphate system has been evaluated for plating copper on silicon for potential micro-electro-mechanical systems (MEMS) applications [M. Cerisier, K. Attenborough, J. Fransaer, C. Van Haesendonck and J.-P. Celis, *J. Electrochem. Soc.* **146**, 2156 (1999)]. In this case, however, copper was plated directly on the silicon surface without the barrier and seed layers needed to fabricate integrated circuits in the Damascene process. Deposition was also performed on a planar surface from a copper pyrophosphate bath at room temperature without organic additives, which would not be suitable for plating trenches and vias in the Damascene process. These workers thoroughly characterized the morphology of the deposits obtained, but did not investigate the capability of the bath for leveling or filling IC features with copper.

For bottom-up filling of narrow Damascene features with relatively high aspect ratios from a complexed copper bath, an additive that substantially accelerates the copper electrodeposition rate is needed. In this case, accelerated deposition at the feature bottom would be provided by the increase in additive concentration resulting from curvature in the copper deposit.

SUMMARY OF THE INVENTION

This invention provides an electroplating bath based on a strongly complexing anion and an accelerating additive for electrodepositing copper circuitry in Damascene trenches and
5 vias on semiconductor chips. This bath avoids the disadvantages of the acid copper sulfate baths employed for Damascene plating in the prior art. Use of a strongly complexing anion (pyrophosphate or cyanide, for example) to suppress runaway copper electrodeposition and improve the deposit properties eliminates the need for the polymeric suppressor additive used in acid copper sulfate baths, and avoids interference from breakdown products thereof.
10 Bottom-up filling of Damascene features is provided by a single accelerating additive species. This additive is present at low concentrations and is not rapidly consumed in the copper electrodeposition process so that organic breakdown products are minimal. The low accelerating additive concentration used and the inherently good throwing power of strongly complexed baths tend to provide a uniform “overburden” layer, which is more easily
15 removed by chemical mechanical planarization (CMP) and obviates the need for the “leveler” additive employed in acid copper sulfate baths. The strongly complexing anion is present in high concentration and is not rapidly consumed in the electrodeposition process, which facilitates control of the plating system.

In addition, the strongly complexed copper electroplating baths of the present
20 invention provide relatively fine-grained deposits that have stable properties, whereas acid copper sulfate deposits are generally large-grained and must be annealed to stabilize key deposit properties (e.g., hardness and electrical conductivity). The fine-grained deposits from the strongly-complexed bath of the invention also tend to be harder and more resistant to dishing during CMP processing. The properties of fine-grained deposits also tend to be much
25 less dependent on the substrate properties so that variations and flaws in the seed and barrier layers used in the Damascene process tend to be less important. Furthermore, the strongly complexing anion used in the bath of the present invention stabilizes the copper ions so that the bath can operate at an alkaline pH (without precipitation of copper hydroxide), which minimizes copper seed layer attack.

A preferred copper plating bath according to the present invention is copper pyrophosphate and a preferred accelerating additive is the 2,5-dimercapto-1,3,4-thiadiazole monomer at a concentration of less than 5 μM . The 2,5-dimercapto-1,3,4-thiadiazole dimer has previously been employed as a brightening/leveling additive in copper pyrophosphate plating baths used for printed wiring board (PWB) applications. For PWB plating, the 2,5-dimercapto-1,3,4-thiadiazole (DMTD) monomer is typically added to the plating bath at a sufficiently high concentration (typically about 15 μM) to form a substantial concentration of the DMTD dimer, which may be detected via the substantial decrease in the copper electrodeposition rate produced. For the preferred copper pyrophosphate bath according to the present invention, the concentration of DMTD monomer is maintained below the concentration required to produce a substantial concentration of the DMTD dimer. In this case, the effect of the monomer on the copper electrodeposition rate is dominant, as indicated by an increase in the copper electrodeposition rate upon addition of a small amount of the DMTD monomer. Bottom-up filling of narrow Damascene features (0.2 μm) without voids or defect lines was demonstrated using a copper pyrophosphate bath containing the accelerating DMTD additive.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the effect of additions of DMTD monomer on the CVS copper electrodeposition rate parameter (A_r/A_s) measured after 16 hours equilibration at 55°C for a copper pyrophosphate bath (pH 8.3) containing 22.5 g/L Cu^{2+} ion, 175 g/L $\text{P}_2\text{O}_7^{4-}$ ion, and 2.25 g/L NH_3 (added as NH_4OH solution). The CVS measurements were made at a Pt rotating disk electrode (4 mm diameter, 2500 rpm) cycled at 50 mV/s between -0.700 and $+1.000$ V vs. saturated calomel electrode (SCE).

Figure 2 depicts the equilibria involved in copper complexing and dimerization of the 2,5-dimercapto-1,3,4-thiadiazole additive.

Figure 3 depicts the Damascene copper electrodeposition process via cross-sections showing: (A) feature (trench or via) without electrodeposited copper; (B) initial stage of copper deposition with curvature developed at feature bottom; (C) partially-filled feature; and (D) fully-filled feature with copper overburden.

Figure 4 depicts a cross-section of a Damascene copper deposit containing a void resulting from conformal deposition rather than bottom-up filling.

Figure 5 shows the effect of additions of DMTD monomer on the CVS copper electrodeposition rate parameter (A_r/A_s) measured at two electrode rotation rates (1000 and 2500 rpm) for the solution of Fig. 1 with 0.50 g/L Triton[®]-X surfactant added. Other measurement conditions were the same as for the Fig. 1 data.

Figure 6 shows an electron micrograph of a cross-section of Damascene vias (0.13 μm wide) that were completely filled with copper from a copper pyrophosphate bath (55°C) containing 2.0 μM (0.3 ppm) DMTD additive.

10 DETAILED DESCRIPTION OF THE INVENTION

Technical terms used in this document are generally known to those skilled in the art. The terms "electroplating", "plating" and "electrodeposition" are equivalent. The term "electrode potential", or simply "potential", refers to the voltage occurring across a single electrode-electrolyte interface, whereas a "cell voltage" is the total voltage applied between two electrodes. In practice, the electrode potential often includes an appreciable resistive voltage drop in the electrolyte, which typically remains constant and does not affect voltammetric results. A "cyclic voltammogram" is a plot of current or current density (on the y-axis) versus the working electrode potential (on the x-axis) typically obtained by cycling the working electrode potential with time between fixed negative and positive limits. A "potentiostat" is an electronic device for controlling the potential of a working electrode by passing current between the working electrode and a counter electrode so as to drive the working electrode to a desired potential relative to a reference electrode.

The term "bath" denotes an electrolytic solution used for electroplating. A copper plating bath based on strongly complexing anions is termed a "complexed bath" or "complexed copper bath" herein. The plural term "anions" encompasses both anions of different types (e.g., pyrophosphate or cyanide), as well as the plurality of anions of the same type that are generally present in a solution of a given anion. The singular term "anion" denotes an anion of a particular type. The term "copper ions" encompasses both Cu^{2+} and Cu^+ species. The dominant species in a complexed copper bath may be either Cu^{2+} or Cu^+ but both species may be present in various complexes with anions, and Cu^+ is generally formed

as an intermediate during copper electrodeposition from the Cu^{2+} species. The term “overpotential” refers herein to the increase in negative electrode potential required to produce substantial copper electrodeposition for a complexed copper bath compared to that required for an acid copper sulfate bath (in the absence of organic additives). An
5 “accelerating additive” substantially enhances the copper electrodeposition rate at a given cathode potential. Damascene “features” include both trenches and vias. The symbol “ \underline{M} ” means molar concentration, and “ $\mu\underline{M}$ ” means micromolar concentration.

This invention provides an electroplating bath based on a strongly complexing anion and an accelerating additive for electrodepositing copper circuitry in trenches and vias on
10 semiconductor chips as part of the Damascene process. Complexing the copper ions via an intrinsic component of the bath provides an inherently high overpotential for copper deposition, which eliminates the need for the suppressor additive and the associated complicated additive system used in acid copper sulfate baths. For example, the onset potential for copper deposition from a copper pyrophosphate bath is typically about -0.5 V
15 greater than that for deposition from an acid copper sulfate bath (without organic additives). In addition, complexed copper systems provide fine-grained deposits which are typically much harder than the large-grained acid sulfate copper deposits, and which exhibit stable mechanical properties that do not change with time. The mechanical properties and texture of the fine-grained deposits produced by complexed baths are also much less substrate
20 dependent than those produced by acid copper sulfate baths, which minimizes the effects of variations and flaws in the barrier and seed layers.

Although complexed copper baths offer significant advantages for Damascene plating, the prior art does not identify a suitable organic additive providing good deposit properties and the accelerated copper deposition needed for bottom-up filling of fine
25 features. Only additives that further suppress (decelerate) the copper electrodeposition rate are reported for such baths in the prior art literature. Suppressor additives can provide bottom-up filling only if a difference in solution mass transport can be established within the feature (between the feature top and bottom), by bath agitation or other solution mass transport means. For fine features (0.2 μm or less in width) or those with relatively high
30 aspect ratios ($>5:1$), the plating solution is practically stagnant within at least a substantial

portion of the feature so that bottom-up filling cannot be attained with the decelerating additives used for complexed copper baths in the prior art.

At a minimum, the plating bath of the present invention must include water as a solvent, copper ions (in either the +1 or +2 oxidation state, or a mixture of the two states),
5 anions that strongly complex the copper ions so as to substantially increase the overpotential for copper electrodeposition such that the copper deposition rate at a given cathode potential is substantially suppressed, and an organic additive compound that tends to accelerate the copper electrodeposition rate. The plating bath may also include one or more cations other than copper ions, auxiliary complexing agents, non-complexing anions, additives to increase
10 the maximum usable current density, and surfactants as wetting agents to aid in wetting the substrate and/or copper surface.

In complexed copper plating baths, a stoichiometric excess of complexing anions to copper ions is typically present to enhance the stability of the copper complex so as to adequately suppress the copper electrodeposition rate and enhance the overall bath stability.
15 This stoichiometric excess of anions is usually provided by addition of a salt of a metal other than copper that readily dissociates in the bath (does not readily form a complex with the anion). The metal cations other than copper ions derived from addition of such a salt (K^+ and Na^+ ions, for example) are typically not electroactive at the potential used for copper electrodeposition, such that relatively pure copper metal is deposited. Alternatively, the salt
20 used to provide excess complexing anions may contain non-metallic cations, e.g., ammonium ions (NH_4^+), to avoid the presence of metallic ions other than copper in the bath, which might degrade device performance if not completely removed after the plating operation. Ions of an electrodepositable metal other than copper can also be added to the plating bath, such that an alloy deposit is obtained. Possible metals for this purpose include silver, zinc, cadmium,
25 iron, cobalt, nickel, tin, lead, bismuth, antimony, gallium and indium. In this case, the metal other than copper may be selected, for example, to increase the resistance of the alloy to electromigration.

Complexing anions that may be used to practice the present invention include pyrophosphate, cyanide, citrate, tartrate, phosphate, glycerolate, ethylenediaminetetraacetic
30 acid (EDTA), carboxylic acids, amines (e.g., triethanolamine), phosphonates, and mixtures thereof. The efficacy of these complexing agents is expected to vary and to depend on the pH

of the plating solution. The pyrophosphate and cyanide anions are preferred since they have been widely used for copper plating. The copper pyrophosphate system is most preferred since cyanide baths are undesirable for environmental and safety reasons. Copper pyrophosphate baths with decelerating organic additives were previously used extensively for circuit board plating, but were largely replaced by acid copper sulfate baths, primarily because the alkaline copper pyrophosphate system is more susceptible to contamination by water soluble organic coatings, which were adopted for environmental reasons. Such water soluble coatings are typically not present during chip plating by the Damascene process.

A preferred electroplating bath for practicing the present invention is copper pyrophosphate containing 1 to 5 μM 2,5-dimercapto-1,3,4-thiadiazole (DMTD) as an accelerating additive. According to the prior art literature [C. Ogden and D. Tench, J. Electrochem. Soc. 128, 539 (1981)], DMTD reacts in copper pyrophosphate baths at the operating temperature (50 – 60°C) to form the DMTD dimer, which is a decelerating additive species that acts as a brightening and leveling agent. The prior art also indicates that the accelerated copper deposition produced by the DMTD monomer species is detrimental to the deposit properties and uniformity, causing protrusions in the deposit to grow faster than recessed areas [D. Tench and C. Ogden, J. Electrochem. Soc. 125, 1218 (1978)]. The printed wiring board plating problem known as “foldback” has been shown to result from accelerated copper deposition at protrusions within through-holes when the DMTD concentration is too low for formation of enough dimer to suppress the copper deposition rate and level the deposit. Thus, the prior art teaches away from use of the DMTD monomer as an additive in copper pyrophosphate baths. We have discovered, however, that the DMTD monomer at an appropriately low concentration provides bottom-up filling of fine Damascene trenches and vias.

Figure 1 shows the effect of additions of DMTD monomer on the CVS copper electrodeposition rate parameter (A_r/A_s) measured in a copper pyrophosphate bath at 55°C. The accelerating effect of the DMTD monomer is evident from the initial increase in A_r/A_s with increasing DMTD concentration. The peak and decrease in A_r/A_s at higher concentrations result from formation of the DMTD dimer, which decelerates the copper electrodeposition rate. In prior art copper pyrophosphate baths, the DMTD concentration has always been maintained at a relatively high value, typically about 15 μM (2 ppm) [C. Ogden

and D. Tench, *Plating Surf. Fin.* **66**(9), 30 (1979)], at which the dominant additive species is the dimer and leveling/brightening is provided by the suppression-depletion mechanism. In the copper pyrophosphate bath of the present invention, the DMTD concentration is maintained at a value below $5\ \mu\text{M}$ for which the dominant additive species is the monomer so that bottom-up filling of Damascene features is attained. The DMTD was added as the protonated DMTD species for which 1.5 mg/L corresponds to $10\ \mu\text{M}$ concentration. The DMTD may also be added as a salt of another cation, sodium or potassium ion, for example.

Figure 2 depicts the chemical equilibria involved in copper complexing and dimerization of the DMTD additive. The key to the strong accelerating effect of the DMTD species is its ability to complex copper ions via two mercapto-groups, which assist in deposition of two contiguous copper atoms that form a new copper nucleus [C. Ogden and D. Tench, *J. Electrochem. Soc.* **128**, 539 (1981)]. The compound (2-amino-5-mercapto-1,3,4-thiadiazole) resulting from substitution of a copper-complexing amino-group for one of the DMTD mercapto-groups also accelerates the copper deposition rate in copper pyrophosphate baths, whereas the compound (2-methyl-5-mercapto-1,3,4-thiadiazole) resulting from substitution of a non-complexing methyl-group does not act as an accelerating additive. Relatively reversible adsorption via the sulfide group (-S-) allows the same DMTD molecule to assist in formation of numerous copper nuclei, which strongly accelerates copper deposition. The dimer species can also complex copper via two mercapto-groups but, in this case, the complexed copper ions are far apart and irreversible adsorption via the disulfide group (-S—S-) serves to block growth sites and decelerate copper deposition. Since an equilibrium is involved, both the monomer and dimer are always present but at sufficiently low DMTD concentrations ($<5\ \mu\text{M}$) the equilibrium strongly favors the monomer, which exerts the dominant effect, accelerating the copper electrodeposition rate.

A standard curve of a CVS rate parameter vs. additive concentration, such as the one shown in Fig. 1 for the DMTD additive, can be used to identify suitable accelerating additive species and concentration ranges for practicing the present invention. Use of a plot of A_s vs. additive concentration might seem to be more appropriate (to simulate stagnant conditions within fine Damascene features) but in this case the effects of species such as the DMTD dimer, which is rapidly consumed during copper deposition, would be masked. For the DMTD additive, A_s continues to increase at higher DMDT concentrations for which

electrode rotation (solution agitation) would produce a decrease in the copper deposition rate via DMTD dimer replenishment at the cathode surface. Consequently, plots of A_r/A_s (or A_r) vs. additive concentration are preferred for identifying suitable accelerating additives and additive concentration ranges for the present invention.

Suitable accelerating additives produce an increase in the CVS rate parameters (A_r , A_s and A_r/A_s), or another parameter reflecting the copper electrodeposition rate, with increasing additive concentration. Excessively high copper deposition rates, produced by higher additive concentrations, can result in unacceptable deposit properties [C. Ogden, D. Tench and J. White, *J. Appl. Electrochem.* **12**, 619 (1982)] and should be avoided. In identifying a suitable additive concentration, the effects of differences in current density and solution mass transport between the copper deposition rate measurements and the bath operating conditions should be considered. The positive slope, and any peak and negative slope associated with dimerization or another additive reaction, for plots of measured copper deposition rate vs. additive concentration generally depend on current density and solution mass transport. A preferred procedure is to empirically determine the optimum additive concentration by plating actual test samples at additive concentrations in the range for which the copper deposition rate increases with increased additive concentration. Numerous organic compounds containing sulfur, nitrogen and/or phosphorus atoms may provide the accelerated copper deposition in complexed copper baths needed for bottom-up filling of fine Damascene features.

By analogy with DMTD, compounds having two mercapto-groups in close proximity on a hetero-ring structure (2,6-dithiopurine, for example) are likely to function as accelerating additives in complexed copper baths. Some di-mercapto-compounds that do not involve a hetero-ring structure (2,3-dimercapto-1-propanol, for example) may also accelerate copper electrodeposition. By analogy with 2-amino-5-mercapto-1,3,4-thiadiazole, compounds for which amino-groups are substituted for one or both of the mercapto-groups in dimercapto-compounds may also be useful as accelerating additives.

Figure 3 depicts cross-sections illustrating bottom-up filling by an accelerating additive in the Damascene process. As shown in Fig. 3(A), Damascene feature 101 (with sidewalls 102 and bottom 103) in semiconductor dielectric material 104 initially has a barrier layer 105 and a copper seed layer 106, and the bottom edges of feature 101 (intersection of

sidewalls 102 and bottom 103) are relatively sharp. The accelerating additive species may adsorb uniformly over copper seed layer 106, or adsorb preferentially at the sharp bottom edges of feature 101. As shown in Fig. 3(B), curved surfaces 108 develop along the bottom edges of copper deposit 109 during the early stages of copper electrodeposition due to simultaneous deposition on the sidewalls 102 and bottom 103, and possibly preferential adsorption of the accelerating additive along the sharp bottom edges of feature 101. Curved surfaces 108 on copper deposit 109 have reduced surface areas compared to the corresponding regions of the sharp bottom edge of feature 101 so that the concentration of adsorbed accelerating additive species, which is not rapidly consumed in the copper deposition process, is increased. This accelerates the copper deposition rate near the bottom 103 of feature 101, which initiates bottom-up filling. As shown in Fig. 3(C), curvature in copper deposit 109 eventually extends across the bottom 110 of copper deposit 109, which further accelerates bottom-up filling. As shown in Fig. 3(D), the Damascene feature is completely filled with copper deposit 109, without a void or defect line, and a layer of copper overburden 110 is deposited. Overburden 110 is subsequently removed via CMP processing.

Figure 4 depicts a cross-section of the Damascene copper deposit obtained by conformal copper electrodeposition rather than bottom-up filling. In this case, copper deposit 301 has a void 302 and/or a defect line 303, which are typically formed when the copper deposits on opposing sidewalls of the feature grow together.

The present invention can be effectively practiced using standard copper pyrophosphate bath formulations [J. W. Dini, Modern Electroplating, 4th Edition, John Wiley & Sons, Ed. M. Schlesinger and M. Paunovic, Chap. 2, Part D (2000)] with the addition of an accelerating additive (which is not used in prior art bath formulations). Copper pyrophosphate plating baths typically contain 22 - 38 g/L copper ions (Cu^{2+}), 150 - 250 g/L pyrophosphate ions [$(\text{P}_2\text{O}_7)^{4-}$], and 1 - 3 g/L ammonia (NH_3). The optimum ratio of $(\text{P}_2\text{O}_7)^{4-}$ to Cu^{2+} is in the 7:1 to 8:1 range, which provides maximum bath stability and good deposit properties. Ammonia serves as an auxiliary complexing agent, which aids in copper anode dissolution. Addition of 5 - 10 g/L nitrate ions (NO_3^-) may be beneficial for improving the maximum usable current density. Typically, copper ions are added as the copper pyrophosphate salt ($\text{Cu}_2\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$), and nitrate and excess pyrophosphate are added as the potassium, sodium or ammonium salts. Ammonia may be added as the gas (NH_3) or as

ammonium hydroxide (NH_4OH). The bath pH is adjusted by addition of phosphoric acid or the hydroxide of potassium, sodium or ammonia to maintain a target value in the pH 8.0 - 8.8 range (typically around pH 8.3). Best results are obtained by operating the bath at 50 - 60°C (typically 55°C). Temperatures higher than 60°C tend to cause rapid decomposition of pyrophosphate to orthophosphate. The concentration of orthophosphate $[(\text{HPO}_4)^{2-}]$ should be maintained at less than 110 g/L by diluting or periodically dumping the bath.

Another feature of the present invention is the use of a surfactant to improve wetting within small Damascene features. Surfactants are usually employed in acidic plating baths for depositing less noble metals (nickel, for example) to help dislodge hydrogen gas bubbles formed as a side reaction during the metal deposition process. Complexed copper plating baths typically operate with substantially 100% current efficiency so that hydrogen bubble formation is not an issue. Complexed copper baths of the prior art have generally not employed surfactants or wetting agents. For Damascene plating, however, a surfactant may be useful to help dislodge air bubbles entrapped within small features when the semiconductor wafer is introduced into the plating solution, particularly in the face-down configuration. A significant concern is that the surfactant might substantially interfere with the functioning of the accelerating additive. We have discovered, however, that a surfactant may be used in the electroplating bath of the present invention, which employs an accelerating additive.

Figure 5 shows the effect of additions of DMTD monomer on the CVS copper electrodeposition rate parameter (A_r/A_s) measured at 1000 and 2500 rpm in a copper pyrophosphate bath (55°C) containing 0.5 mg/L polyoxyethylene(10)isooctylphenylether (sold commercially as Triton[®] X-100) as a surfactant. As seen by comparing Figs. 1 and 5, the behavior with and without the surfactant added is substantially the same in the low additive concentration range corresponding to increased copper deposition rate with increased DMTD concentration (note scale difference for x-axis). This indicates that a surfactant may be used in the complexed copper bath of the present invention to improve wetting within Damascene features. At higher DMTD concentrations, the surfactant produces a relatively precipitous decrease in copper deposition rate, apparently by augmenting the effect of the DMTD dimer suppressor species. In the additive concentration range useful for

the present invention ($<5 \mu\text{M}$), the electrode rotation rate (1000 or 2500 rpm) used for CVS measurements has little effect on A_r/A_s vs. DMTD concentration plots.

A wide variety of surfactants could be used within the scope of the present invention to improve wetting in small Damascene features. Preferably, the surfactant is substantially stable against cathodic decomposition, so that good deposit properties are obtained and excessive amounts of detrimental contaminants are not formed. The Triton[®] surfactants have been widely used as a polarographic maximum suppressors and are known to be stable at substantial cathodic potentials. Surfactants typically employed in baths for electrodepositing nickel (and other less-noble metals) that could be used in complexed copper baths include sodium lauryl sulfate and sodium dodecyl sulfate.

The teachings of the prior art counsel against the approach of the present invention. The fine-grained deposits provided by complexed copper baths are reported to exhibit poor resistance to electromigration [e.g., C. Ryu, K. Kwon, A. L. S. Loke, J. M. Dubin, R. A. Kavari, G. W. Ray, and S. S. Wong, Symp. on VLSI Tech. (June 8-11, 1998)]. Early work [e.g., T. Nitta, J. Electrochem. Soc. 140, 1131 (1993)] showed that acid sulfate copper deposits have a higher activation energy for electromigration after annealing, which increases the grain size. Acid sulfate copper deposits are routinely annealed for Damascene applications, to enhance electromigration resistance and to stabilize the properties for more consistent CMP results. Other studies compared large-grained acid sulfate copper deposits with vacuum-deposited or chemical-vapor-deposited (CVD) materials, which are of only moderate grain size, and found that the large-grained deposits have higher resistance to electromigration.

Contrary to these teachings, the inventors believe that the fine-grained deposits obtained from complexed copper baths will prove to have good electromigration resistance. The poor electromigration resistance observed for CVD copper materials of moderate grain size may be attributed to micro-voids (indicated by less than theoretical density). On the other hand, deposits from strongly complexed baths (e.g., copper pyrophosphate) containing organic additives typically approach theoretical density (indicating minimum void volume), and are extremely fine-grained. Furthermore, the high density of the "necks" which connect the crystallites together in such deposits should actually inhibit copper atom motion and impede electromigration. Our preliminary tests indicate that the electromigration resistance

of deposits from copper pyrophosphate baths can be at least as high as deposits from acid copper sulfate baths.

The complexed copper plating bath of the present invention offers significant advantages in terms of both simplicity and performance compared to the acid copper sulfate bath. A major advantage is that the single accelerating additive species employed in the complexed bath can readily be controlled to provide bottom-up filling, whereas the acid copper sulfate system used for Damascene plating in the prior art requires a complicated additive system that is difficult to control. Additive-additive interactions and the dynamic balance required between consumption and mass transport limit the efficacy of acid copper sulfate baths for Damascene plating of narrow features with high aspect ratios. The effective concentration of the DMTD additive in the copper pyrophosphate bath can be determined by CVS via a simple A_r/A_s measurement [D. Tench and C. Ogden, J. Electrochem. Soc. 125 (2), 194 (1978)]. This additive is present at low concentrations and is not rapidly consumed in the copper electrodeposition process so that organic breakdown products are minimal, whereas breakdown products of the suppressor and anti-suppressor additives must be frequently diluted in acid copper sulfate baths to avoid degradation of the deposit quality. Another advantage of complexed copper baths is that the additive can be a known compound (e.g., DMTD) rather than a proprietary formulation, which allows the user to exercise better control of the plating process. Furthermore, attack of copper seed layers, which is a problem for acid copper sulfate baths, is minimized for alkaline complexed copper baths.

In addition, the low accelerating additive concentration used and the inherently good throwing power of complexed copper baths tend to provide a uniform “overburden” layer, which is more easily removed by chemical mechanical planarization (CMP) and obviates the need for the “leveler” additive employed in acid copper sulfate baths. In addition, the fine-grained deposits provided by complexed copper baths tend to have stable properties that are relatively insensitive to the substrate, whereas annealing is required to stabilize the properties of acid copper deposits, which tend to depend strongly on the substrate. The fine-grained deposits from complexed copper baths also tend to be about twice as hard as those from acid copper sulfate baths so that dishing during CMP processing is less of an issue. The resistivity of pyrophosphate and annealed acid sulfate copper deposits are equivalent.

The simple accelerating additives used in the complexed copper bath of the present invention also tend to be less sensitive to degradation by ac voltages and are therefore more amenable for use with pulse plating or periodic reverse pulse plating to enhance the deposit properties or overall plating rate. In contrast, organic additives of the types typically employed in acid copper sulfate baths tend to be consumed at a much faster rate under alternating current (ac) conditions, making control of additive concentrations and bath purity more difficult. This restricts the options in terms of additive types and operating conditions for pulse plating from acid sulfate systems.

Although the plating bath of the present invention is discussed herein with respect to the Damascene process for making copper integrated circuits on semiconductor chips, this bath should also be useful for a wide variety of applications. For example, the bath could be applied to fabrication of micro-electro-mechanical systems (MEMS) devices, and especially those involving integration with electronic devices. This bath is particularly useful for bottom-up filling of small “blind” features. Any use of the bath of this invention is explicitly claimed.

Description of a Preferred Embodiment

Damascene copper plating with the bath of the present invention can be performed in a laboratory apparatus, or with a commercial plating tool (may need to be modified for operation at elevated temperature). Good results are obtained by rotating the wafer during plating and/or providing a uniform laminar flow of solution over the wafer surface via pumping the solution through a nozzle system. The wafer holder should have a seal designed to avoid solution contact with the electrical contact made to the copper seed layer around the periphery of the wafer side to be plated. The holder should be designed to have a low profile and/or other means for avoiding disruption of laminar flow over the wafer surface. Pumped solution from a nozzle is typically directed toward the center of the rotating wafer, but could be directed toward other wafer locations. Plating may also be performed from a stagnant plating bath.

The preferred electroplating bath for practicing the invention is a copper pyrophosphate bath containing 22 - 38 g/L copper ions (predominantly Cu^{2+}), 150 - 250 g/L pyrophosphate ions $[(\text{P}_2\text{O}_7)^{4-}]$, 1 - 3 g/L ammonia (NH_3), 1 - 5 μM 2,5-dimercapto-1,3,4-

thiadiazole (DMTD), and optionally 5 - 10 g/L nitrate ions (NO_3^-). Copper ions are preferably added as the copper pyrophosphate salt ($\text{Cu}_2\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$), and nitrate and excess pyrophosphate are preferably added as the potassium, sodium or ammonium salts. Addition as ammonium pyrophosphate is preferred to avoid the possibility of integrated circuit degradation by sodium or potassium ions. Ammonia may be added as the gas (NH_3) or as ammonium hydroxide (NH_4OH). The bath pH is preferably maintained at about pH 8.3 by addition of phosphoric acid or the hydroxide of potassium, sodium or ammonia. The bath temperature should be maintained in the 50 - 60°C range, preferably near 55°C. The concentration of orthophosphate [HPO_4^{2-}] should be maintained at less than 110 g/L by diluting or periodically dumping the bath.

The efficacy of the invention for Damascene plating was demonstrated by copper plating coupons (typically 2 cm square) cut from an eight-inch-diameter silicon wafer coated with a metal nitride barrier layer and a copper seed layer. The wafer contained vias 0.13 μm wide (5.4:1 aspect ratio), vias 0.2 μm wide (4:1 aspect ratio), trenches 0.33 μm wide (2:1 aspect ratio), and trenches 0.38 μm wide (0.7:1 aspect ratio). Copper was plated at 35 mA/cm^2 to an average thickness of 1.0 μm in a 600-mL beaker containing a copper anode (2 cm square) and 500 mL of plating solution maintained at 55°C on a hot plate. The copper pyrophosphate plating solution contained 23.5 g/L copper ion (Cu^{2+}), 176.3 g/L pyrophosphate ion [$\text{P}_2\text{O}_7^{4-}$], 2.1 g/L ammonia (NH_3), 7.4 g/L nitrate ion (NO_3^-), and various concentrations of 2,5-dimercapto-1,3,4-thiadiazole (DMTD). The solution pH was adjusted to 8.2 by addition of phosphoric acid. In some cases, 0.50 g/L Triton[®]-X was added as a surfactant. During plating, the coupon and the anode were held vertically near the sides of the beaker (8 cm apart) and the solution was stirred with a Teflon-coated magnetic stir bar (200 rpm).

Coupons were mechanically cleaved and cross-sections were examined by scanning electron microscopy (SEM) in the as-cleaved state. For each plating condition, 10 to 20 Damascene features of each type were examined for bottom-up filling, except when the cleave lines did not intersect a sufficient number of features of a given type. In some cases, defects in the copper deposit resulting from extraneous causes were observed. In particular, lack of plating on a portion of some feature side walls apparently resulted from poor wetting and/or high electrical resistance of the copper seed layer due to oxidation. This was evident

since a prior electrochemical reduction in borate buffer solution (pH 8.3) was shown to reduce the incidence of this type of defect. Such oxidation is likely to have occurred since the wafers available at the time had been stored in air for several months. Other sporadic defects observed for copper deposits, especially within fine features, most probably resulted from the poorly controlled beaker plating process and the crude cross-sectioning procedure used. Mechanical cleaving is known in the art to sometimes introduce voids associated with “pull away” of a portion of the deposit. Because of the extraneous factors affecting the quality of the Damascene copper deposit, good bottom-up filling was judged to have been attained when the majority of the features were filled with copper exhibiting no voids or defect lines. Plating conditions shown to provide good bottom-up filling should yield low defect rates for a properly controlled production wafer plating process involving fresh copper seed layers.

Example 1—Coupons were plated from copper pyrophosphate solutions (55°C) containing 0.0, 0.33, 0.67, 1.0, 1.3, 1.7, 2.0, 2.3, 3.3, 5.0 or 8.3 μM of the DMTD additive (without surfactant added). Good bottom-up filling of the smallest features (0.13 μm vias) was attained with the 2.0 μM solution, as indicated by the micrograph in Figure 6. Good bottom-up filling of all of the larger features (0.20, 0.33 and 0.38 μm wide) was attained with the 1.3, 1.7 and 2.0 μM solutions. Incomplete filling was observed for all features with all of the other solutions, except that good bottom-up filling was observed for the two larger features (0.33 and 0.37 μm wide) with the 3.3 μM solution. These data show that the DMTD monomer additive of the present invention provides good bottom-up filling of Damascene features as fine as 0.13 μm wide (5.4:1 aspect ratio). The optimum DMTD concentration was about 2 μM for the conditions used but would be expected to depend on the plating parameters, such as current density, solution composition, and solution mass transport.

Example 2—Coupons were plated from copper pyrophosphate solutions (55°C) containing 0.50 g/L Triton[®]-X surfactant and 0.0, 0.33, 0.67, 1.0, 1.3, 1.7, 2.0, or 5.7 μM of the DMTD additive. As was the case without surfactant added, a DMTD concentration of about 2 μM provided good bottom up filling of even the smallest Damascene features (0.13 μm vias) in the presence of the Triton[®]-X surfactant.

The preferred embodiments of this invention have been illustrated and described above. Modifications and additional embodiments, however, will undoubtedly be apparent to those skilled in the art. Furthermore, equivalent elements may be substituted for those

illustrated and described herein, parts or connections might be reversed or otherwise interchanged, and certain features of the invention may be utilized independently of other features. Consequently, the exemplary embodiments should be considered illustrative, rather than inclusive, while the appended claims are more indicative of the full scope of the

5 invention.